

Mesoporous Vanadium Oxide as Cathodes for Lithium Batteries

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Since the discovery of MCM-41 silica in 1992 which was synthesized by using a molecular self-assembly technique to direct the formation of a mesoporous silica network [1], much work has been performed to extend the same approach to transition metal oxides which are of interest as catalysts, electronic materials, and battery electrodes. Major progress has been recently accomplished by using non-ionic polymer surfactants as templates and a wide variety of metal oxides (including Ti, Nb, Ta, W, Zr, and Al oxides and their mixed oxides) have been synthesized [2]. The templates can be removed either by solvent extraction or by thermal treatment. However, information on the applications of these materials has been very limited. Recently, mesoporous tungsten oxide has exhibited great promise as an improved electrochromic material with enhanced kinetic performance [3].

In consideration of ion insertion materials, which are important for electrochromic devices and lithium batteries, there has always been a need for developing highly porous materials to improve the rate capability. This improvement translates to increasing the switching speed of an electrochromic device or the power density of a lithium battery. It is well established that the kinetics of these devices is limited by solid state ion diffusion. Reducing the length of the diffusion path by designing a highly porous network is a desirable approach to address this issue. In the case of vanadium oxide, aerogels and similar materials have been synthesized and evaluated in lithium batteries that have shown improvement in kinetic performance. Another approach is to use the templating method, i.e., fabricate a negative replica of nanoporous materials such as an anodized alumina membrane.

We have employed the molecular assembly templating approach to synthesize mesoporous vanadium oxide. The vanadium oxide deposit formed by electrolysis of the solution containing the copolymer surfactant is mesoporous, as evidenced by transmission electron microscopy (TEM). The material exhibits wormhole-like pore structures with no apparent long-range order. Pores in the vanadium oxide material presumably originate from the region previously occupied by polymer surfactants. Despite the lack of long-range order and the absence of any peaks in the X-ray diffraction (XRD) spectrum, the material possesses relatively uniform channel spacings, which are 3 to 4 nm. Complete removal of the polymer surfactants by extraction with water and ethanol was confirmed by energy dispersive X-ray spectroscopy (EDX). In comparison, a control sample prepared in the absence of the polymer surfactant has a dense structure.

We subsequently investigated the performance of mesoporous vanadium oxide as a cathode material in a lithium battery. In particular, the charge/discharge rate capability is of great interest. The designed mesoporous structure should provide a very short diffusion path for lithium ions and permit fast charge and discharge of the electrode. Shown in Figures 1a and 1b are the discharge curves of the mesoporous vanadium oxide and its control

counterpart. C rate is defined as inserting one lithium per V_2O_5 in one hour which corresponds to a current density of 147 mA/g. At a very high rate of 50C at which the electrode discharges in approximately 60 s, the mesoporous material delivers 125 mAh/g (55% of the capacity at a 1C rate) vs 75 mAh/g (40% of the capacity at a 1C rate) by the control sample. Notice that the 50C rate employed in this study is approaching the typical discharge rate for electrochemical capacitors. The capacity of the mesoporous vanadium oxide corresponds to a gravimetric capacitance of 450 F/g, which compares favorably with those of porous carbon double layer capacitors. Consequently, it is possible to use this material for low power capacitors or high power batteries, which bridges the gap between conventional lithium batteries and double layer capacitors.

References

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
2. P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Nature*, **396**, 152 (1998).
3. W. Cheng, E. Baudrin, B. Dunn, J.I. Zink, *J. Mater. Chem.*, **11**, 92 (2001).

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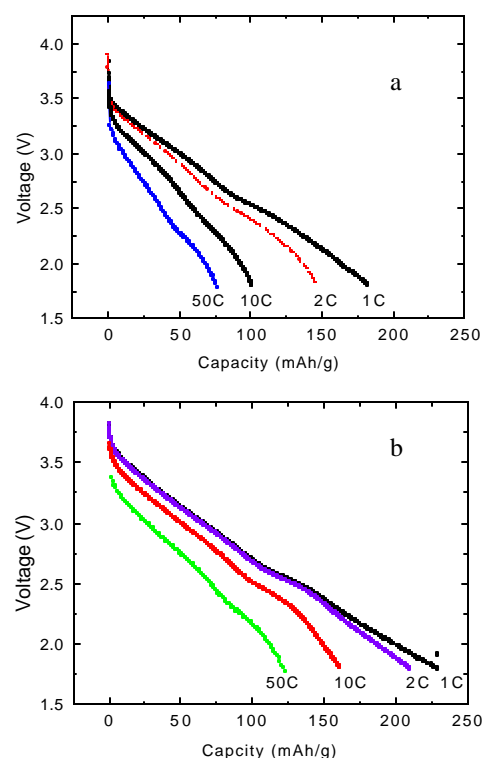


Figure 1. Discharge curves at different rates for electrodeposited vanadium oxide. a (top) control sample; b (bottom) mesoporous vanadium oxide.